

CLAIMS

1. An aqueous bath composition for the electroless deposition of copper molybdenum, comprising, in addition
5 to water:
 - a soluble source of copper ions;
 - a soluble source of molybdenum ions; and
 - a reducing agent comprising boron;wherein said composition is adapted to electrolessly
10 produce a copper molybdenum deposit having a resistivity of less than 30 microhm.cm.
2. A composition according to claim 1, wherein said copper molybdenum deposit has a resistivity of less than
15 10 microhm.cm.
3. A composition according to claim 1, wherein said composition is substantially devoid of alkali metals and alkaline earth metals.
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4. A composition according to claim 1, wherein said soluble source of copper ions comprises copper sulfate.
5. A composition according to claim 4, wherein said
25 copper sulfate comprises copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) at a concentration of 2-10 g/l.
6. A composition according to claim 5, wherein said copper sulfate pentahydrate is at a concentration of 3-5
30 g/l.

7. A composition according to claim 1, wherein said soluble source of molybdenum ions comprises molybdic (5N) acid monohydrate ($H_2 MoO_4 \cdot H_2O$).

5 8. A composition according to claim 7, wherein said molybdic acid monohydrate is present at a concentration of 0-5 g/l.

9. A composition according to claim 8, wherein said
10 molybdic acid monohydrate is present at a concentration of 1.5-3 g/l.

10. A composition according to claim 1, wherein the reducing agent is selected from sodium borohydride,
15 potassium borohydride, borane pyridine complex and a borazane selected from dimethylamineborane (DMAB), borane triethylamine (TEAB), DMAB-complex and TEAB-complex.

11. A composition according to claim 10, wherein said
20 borazane is of the formula $R_x NH_y \cdot BH_{(x+y)}$,

wherein x is an integer between 0 and 3,

wherein y is an integer between 0 and 3, and

wherein R is an organic group selected from methyl and ethyl

25 (SL6).

12. A composition according to claim 10, wherein the reducing agent comprises dimethylamineborane.

30 13. A composition according to claim 12, wherein the reducing agent comprises a dimethylamineborane.complex.

14. A composition according to claim 13, wherein said dimethylamineborane complex is present at a concentration of 5-20 g/l_(7N).

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15. A composition according to claim 14, wherein said dimethylamineborane complex is present at a concentration of 7-12 g/l_(8N).

10 16. A composition according to claim 11, further comprising tetra-methyl ammonium hydroxide (TMAH) at a concentration of 50-100 g/l.

15 17. A composition according to claim 1, further comprising ammonium hydroxide.

18. A composition according to claim 17, wherein said ammonium hydroxide is at a concentration of less than 20 ml/l.

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19. A composition according to claim 1, wherein the pH is between 8-12.

20. A composition according to claim 19, wherein the pH
25 is between 9-11.

21. A composition according to claim 1, wherein said composition is adapted to produce a copper molybdenum deposit having at least one of the following properties:

(i) a change in reliability as defined by mean-time-to-failure during electro-migration testing of more than a factor of ten;

(ii) a void density of less than $0.5/\text{cm}^2$;

5 (iii) a grain boundary diffusion coefficient of less than $10^{-8.3} \cdot e^{-1.25\text{ev}/kT}$;

(iv) a grain boundary diffusion coefficient, D_0 of $10^{-8.3} \text{ cm/s}$; and

10 (v) a distribution of grain sizes having a standard deviation of less than 3 nm.

22. A composition according to claim 1, wherein said composition is adapted to electrolessly deposit copper
15 molybdenum at a temperature of less than 60°C .

23. A composition according to claim 22, wherein said composition is adapted to electrolessly deposit copper molybdenum at a temperature of between 40°C to about
20 50°C .

24. A composition according to claim 1, further comprising a surfactant.

25 25. A composition according to claim 24, wherein said surfactant comprises at least one of RE-610 and Triton X-100(SL9).

26. An aqueous bath composition for the electroless

deposition of copper molybdenum, comprising, in addition to water:

a soluble source of copper ions;

a soluble source of molybdenum ions;

5 a soluble source of citrate ions; and

a reducing agent comprising boron; and

wherein said composition is adapted to electrolessly produce a copper molybdenum deposit having a resistivity of less than 300 microhm.cm.

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27. A composition according to claim 26, wherein said soluble source of citrate ions comprises sodium citrate.

28. A composition according to claim 26, wherein said
15 copper molybdenum deposit has a resistivity of less than 100 microhm.cm.

29. A composition according to claim 26, wherein said composition is substantially devoid of alkali metals and
20 alkaline earth metals.

30. A composition according to claim 25, wherein said soluble source of copper ions comprises copper sulfate.

25 31. A composition according to claim 30, wherein said copper sulfate comprises copper sulfate pentahydrate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$) at a concentration of 2-10 g/l.

32. A composition according to claim 31, wherein said
30 copper sulfate pentahydrate is at a concentration of 3-5 g/l.

33. A composition according to claim 26, wherein said source of molybdenum comprises molybdic (10N) acid monohydrate ($H_2 MoO_4 \cdot H_2O$).

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34. A composition according to claim 33, wherein said molybdic acid monohydrate is present at a concentration of 0-5 g/l.

10 35. A composition according to claim 34, wherein said molybdic acid monohydrate is present at a concentration of 1.5-3 g/l.

36. A composition according to claim 26, wherein the
15 reducing agent is selected from dimethylamineborane (DMAB), sodium hydroborate, potassium hydroborate, sodium borohydride, potassium borohydride, a borazane, and borane pyridine complex.

20 37. A composition according to claim 36, wherein said borazane is of the formula $R_xNH_y \cdot BH_{(x+y)}$,

wherein x is an integer between 0 and 3,

wherein y is an integer between 0 and 3, and

wherein R is an organic group selected from methyl
25 and ethyl

38. A composition according to claim 26, wherein the reducing agent comprises dimethylamineborane.

30 39. A composition according to claim 38, wherein the reducing agent comprises a dimethylamineborane complex.

40. A composition according to claim 39, wherein said dimethylamineborane complex is present at a concentration of 5-20 g/l₍₁₁₈₎.

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41. A composition according to claim 39, wherein said dimethylamineborane complex is present at a concentration of 7-12 g/l₍₁₂₈₎.

10 42. A composition according to claim 26, further comprising tetra-methyl ammonium hydroxide (TMAH) at a concentration of 50-100 g/l.

15 43. A composition according to claim 26, further comprising ammonium hydroxide.

44. A composition according to claim 43, wherein said ammonium hydroxide is at a concentration of less than 20 ml/l.

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45. A composition according to claim 26, wherein the pH is between 8-12.

25 46. A composition according to claim 45, wherein the pH is between 9-11.

30 47. A composition according to claim 26, wherein said composition is adapted to produce a copper molybdenum deposit having at least one of the following properties₍₅₁₃₎:

(i) a change in reliability as defined by mean-time-to-failure during electro-migration testing of more than a factor of ten;

(ii) a void density of less than $0.5/\text{cm}^2$;

5 (iii) a grain boundary diffusion coefficient of less than $10^{-8.3} \cdot e^{-1.25\text{ev}/kT}$;

(iv) a grain boundary diffusion coefficient, D_0 of $10^{-8.3} \text{ cm/s}$; and

10 (v) a distribution of grain sizes having a standard deviation of less than 3 nm.

48. A composition according to claim 26, wherein said composition is adapted to electrolessly deposit copper molybdenum at a temperature of less than 60°C .

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49. A composition according to claim 48, wherein said composition is adapted to electrolessly deposit copper molybdenum at a temperature of between 40°C to about 50°C .

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50. A composition according to claim 26, further comprising a surfactant.

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~~50~~. A composition according to claim 50, wherein said surfactant comprises at least one of RE-610 and Triton X-100.

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~~51~~. A copper molybdenum film electrolessly deposited on a surface from a bath comprising the composition

according to claim 1, and wherein a resistivity of said film is less than 10 microOhm.cm.

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52. A film according to claim ⁵⁰51, wherein the thickness
5 of said film is less than approximately one micron.

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53. A film according to claim ⁵³52, wherein the thickness
of said film is less than approximately 0.1 micron.

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54. A film according to claim ⁵⁰53, wherein a resistivity
of said film is less than 8 microOhm.cm.

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55. A film according to claim ⁵⁰54, wherein said film
comprises 0-3% molybdenum.

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56. A film according to claim ⁵⁶55, wherein said film
comprises 1-3% molybdenum.

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57. A film according to claim ⁵⁰56, wherein said film acts
20 as a diffusion barrier for a metal on said surface;
wherein said metal is selected from copper, gold,
platinum, palladium, silver, nickel, cadmium, indium and
aluminum.

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25 58. A film according to claim ⁵⁰57, wherein said film acts
as an oxidation barrier.

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59. A film according to claim ⁵⁰58, wherein said film acts
as a corrosion barrier.

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⁶¹
60. A copper molybdenum film electrolessly deposited on a surface from a bath comprising the composition according to claim 26, and wherein a resistivity of said
5 film is less than 300 microOhm.cm.

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61. A film according to claim 60, wherein the thickness of said film is less than approximately one micron.

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62. A film according to claim 61, wherein the thickness of said film is less than approximately 0.1 micron.

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63. A film according to claim 60, wherein a resistivity of said film is less than 100 microOhm.cm.

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64. A film according to claim 60, wherein a resistivity of said film is less than 10 microOhm.cm.

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65. A film according to claim 60, wherein said film
20 comprises 0-3% molybdenum.

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66. A film according to claim 60, wherein said film comprises 1-3% molybdenum.

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67. A film according to claim 60, wherein said film acts as a diffusion barrier for a metal on said surface; wherein said metal is selected from copper, gold, platinum, palladium, silver, nickel, cadmium, indium and aluminum.

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68. A film according to claim ⁶¹69, wherein said film acts as an oxidation barrier.

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69. A film according to claim ⁶¹69, wherein said film acts as a corrosion barrier.

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70. A method for the electroless deposition of copper molybdenum on a surface, comprising:

10 electrolessly depositing copper molybdenum on said surface, substantially in the absence of alkali metal ions so as to produce a copper molybdenum layer having a resistivity of less than 300 microhm.cm.

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15 ⁷²
71. A method according to claim ⁷¹70, wherein said resistivity is less than 100 microhm.cm.

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72. A method according to claim ⁷¹71, wherein said resistivity is less than 10 microhm.cm.

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73. A method according to claim ⁷¹72, wherein said resistivity is less than 8 microhm.cm.

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74. A method according to claim ⁷¹73, further comprising activating said surface, and wherein activating said
25 surface occurs at least partially under dry process conditions.

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75. A method according to claim ⁷¹74, wherein said surface comprises silicon.

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76. A method according to claim ⁷¹75, wherein said surface

comprises copper.

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76. A method according to claim 70, wherein activating said surface further comprises depositing at least one metal on said surface.

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78. A method according to claim 76, wherein said at least one metal is selected from aluminum, cobalt, copper and titanium.

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78. A method according to claim 76, and further comprising removing at least partially some of said at least one metal.

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79. A method according to claim 76, further comprising activating said surface, and wherein activating said surface occurs, at least partially, under wet process conditions.

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80. A method according to claim 79, wherein activating said surface comprises at least one of the following steps:

(a) degreasing said surface;

(b) removing at least one oxide from said surface;

- 25 (c) fluoride etching said surface;

(d) rinsing said surface;

(e) activating said surface with palladium; and

(f) pre-dipping said surface in a solution comprising at least one of a reducing agent and a

complexing agent.

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81. A method according to claim ~~70~~⁷¹, wherein said surface comprises silicon.

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82. A method according to claim ~~81~~⁸³, wherein said surface comprises copper.

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83. A method according to claim ~~70~~⁷¹, wherein electrolessly depositing comprises electrolessly depositing a film having a thickness of less than approximately one micron.

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84. A method according to claim ~~83~~⁸⁵, wherein the thickness of said film is less than approximately 0.1 micron.

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85. A method according to claim ~~70~~⁷¹, wherein said film comprises 0-3 % molybdenum.

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86. A method according to claim ~~70~~⁷¹, wherein depositing said copper molybdenum is at a temperature of less than 60°C.

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87. A method according to claim ~~86~~⁸⁸, said temperature is from around 40°C to 50°C.

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88. A method according to claim ~~87~~⁸⁹, wherein depositing said copper molybdenum occurs at a pH of around 9 up to

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~~89~~. A method according to claim ⁹⁰~~88~~, wherein said pH is around 9.5 to 10.5.

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~~90~~. A method for the electroless deposition of copper molybdenum on a surface, comprising:

electrolessly depositing copper molybdenum on said surface in the presence of citrate ions so as to produce a copper molybdenum layer having a resistivity of less than 300 microhm.cm.

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